tained using a Varian Associates A-60 instrument. Melting points were determined on a heated Kofler block. All manipulations of the phosphine ligands were carried out in an atmosphere of nitrogen; unless otherwise specified, the complexes were sufficiently stable to be crystallized without exclusion of air.

Dichlorotetrakis(diethylphosphine)ruthenium(II).—Ruthenium trichloride (0.32 g., 1.24 mmoles), diethylphosphine (0.56 g., 6.20 mmoles), and ethanol (50 ml.) were refluxed for 2 hr. to give a yellow-green solution. After filtration, cooling gave yellow plates of the pure complex (m.p. 175–190°, yield 67%).

Anal. Calcd. for $C_{16}H_{44}Cl_2P_4Ru$: C, 36.1; H, 8.3; Cl, 13.3; mol. wt., 532. Found: C, 36.2; H, 8.0; Cl, 13.3; mol. wt. (C_6H_6), 500.

Dichlorotetrakis(diphenylphosphine)ruthenium(II) was similarly prepared, yellow crystals precipitating from the reaction mixture. Recrystallization from chloroform–hexane gave yellow-orange needles (m.p. 245–255°, with decomposition setting in above 200°, yield 29%).

Anal. Calcd. for $C_{48}H_{44}Cl_2P_4Ru$: C, 62.9; H, 4.8; Cl, 7.7. Found: C, 62.65; H, 4.8; Cl, 6.7.

Trichlorotris(diethylphosphine)rhodium(III).—$RhCl_3 \cdot 3H_2O$ (0.52 g., 1.965 mmoles) in ethanol (50 ml.) was treated with diethylphosphine (0.53 g., 5.9 mmoles) to give an immediate crystalline precipitate. After standing overnight the precipitated solid was filtered and crystallized from nitromethane–methanol to give orange prisms (m.p. 212–215° dec., yield 21%).

Anal. Calcd. for $C_{12}H_{33}Cl_3P_3Rh$: C, 30.05; H, 6.9; Cl, 22.2. Found: C, 30.3; H, 6.5; Cl, 21.4.

Trichlorotris(diphenylphosphine)rhodium(III) (Isomers A and B).—$(C_6H_5)_2PH$ (1.05 g., 5.63 mmoles) was added to a solution of $RhCl_3 \cdot 3H_2O$ (0.50 g., 1.88 mmoles) in ethanol (50 ml.) to give a yellow-brown precipitate which was filtered and dried. The crude product was extracted with hot acetone and addition of hexane to the filtrate precipitated pure isomer A as a yellow-brown microcrystalline powder (m.p. 150–170° dec., yield 40%).

Anal. Calcd. for $C_{36}H_{33}Cl_3P_3Rh$: C, 56.3; H, 4.3; Cl, 13.85; P, 12.1; mol. wt., 768. Found: C, 54.2; H, 4.9; Cl, 13.4; P, 11.8; mol. wt. (CH_2Br_2), 790.

The residue from the acetone extraction was crystallized from chloroform–hexane to give isomer B as pale yellow needles (m.p. 150–170° dec., yield 7%).

Anal. Found: C, 56.4; H, 4.5; Cl, 14.4; P, 11.5; mol. wt. (CH_2Br_2), 528.

Chlorotris(diphenylphosphine)rhodium(I).—$[RhCl(C_2H_4)_2]_2$[3] (0.20 g., 0.355 mmole), diphenylphosphine (0.53 g., 2.84 mmoles), and benzene (20 ml.) were stirred together for 15 hr. to give a slight yellow precipitate and an orange-red solution. After filtration under nitrogen, addition of hexane to the solution caused the slow separation of yellow-brown crystals which were filtered and washed with hexane (m.p. 173–175°, yield 52%).

Anal. Calcd. for $C_{36}H_{33}ClP_3Rh$: C, 62.0; H, 4.8; Cl, 5.1; P, 13.3; Rh, 14.8; mol. wt., 697. Found: C, 61.9; H, 4.7; Cl, 3.4; P, 12.9; Rh, 15.5; mol. wt. (C_6H_6), 680.

Dichlorobis(dimethylphosphine)palladium(II).—Dimethylphosphine was passed into a solution of $[PdCl_2\{P(C_4H_9)_3\}]_2$ (5.0 g., 6.60 mmoles) in dichloromethane (100 ml.) until the orange color faded to pale yellow. Removal of solvent at 15 mm. gave a yellow oil which formed a crystalline solid in acetone. Recrystallization from chloroform–hexane gave colorless prisms (dec. above 230°, yield 35%).

Anal. Calcd. for $C_4H_{14}Cl_2P_2Pd$: C, 15.9; H, 4.7; Cl, 23.5. Found: C, 16.4; H, 5.0; Cl, 23.1.

The acetone washings yielded yellow crystalline $[PdCl_2\{P(C_4H_9)_3\}_2]$. The reaction therefore takes place as follows

$$[PdCl_2\{P(C_4H_9)_3\}]_2 + 2(CH_3)_2PH \longrightarrow [PdCl_2\{HP(CH_3)_2\}_2] + [PdCl_2\{P(C_4H_9)_3\}_2]$$

The mixed complex is apparently unstable, in contrast to $[PdCl_2\{HP(C_2H_5)_2\}PR_3]$, R = C_2H_5, C_6H_5.[2]

Dichlorodi-μ-(dimethylphosphido)bis(dimethylphosphine)-dipalladium(II).—$[PdCl_2\{HP(CH_3)_2\}_2]$ (0.50 g., 1.13 mmoles), *p*-toluidine (0.12 g., 1.13 mmoles), and benzene (50 ml.) were refluxed together for 16 hr. to give a yellow solution and white precipitate. After filtration, the solution was evaporated leaving a yellow oil which crystallized in hexane. Recrystallization from benzene–hexane gave pale yellow needles (m.p. 150–154° dec., yield 45%).

Anal. Calcd. for $C_8H_{26}Cl_2P_4Pd_2$: C, 18.1; H, 4.9; Cl, 13.4; mol. wt., 530. Found: C, 18.4; H, 4.9; Cl, 13.9; mol. wt. (C_6H_6), 532.

The n.m.r. spectrum in $CDCl_3$ shows a singlet at 8.42 τ with a shoulder on the low field side and a doublet at 8.60 τ (J_{HP} = 6.4 c.p.s.). The resonance at 8.42 τ has a shape similar to that observed for the methyl resonance of $(CH_3)_2PH$ (at 8.85 τ) and is thus assigned to the terminal dimethylphosphine ligands. The doublet resonance is therefore due to the methyl groups attached to bridging phosphorus.

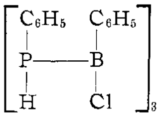
Acknowledgment.—The author thanks Mr. F. S. Humiec for experimental assistance.

Correspondence

Phosphinoarylboranes

Sir:

On the basis of chemical composition, molecular weight, infrared spectra, and chemical reactions, the trimer



$$\left[\begin{array}{ccc} C_6H_5 & & C_6H_5 \\ | & & | \\ P & \text{——} & B \\ | & & | \\ H & & Cl \end{array}\right]_3$$

I

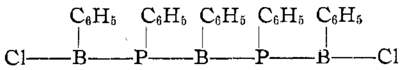
was identified as one of the products from the vacuum distillation of a solution prepared by adding $C_6H_5PH_2$ to a benzene solution containing excess $C_6H_5BCl_2$ and refluxing the mixture until evolution of HCl ceased.

The trimer (I) was a white, waxy solid (yield, about 15%) which sublimed at 60° under vacuum. The cryoscopic molecular weight in benzene was 680 and the chlorine content was 15.6 wt. % compared to the theoretical values of 697 for the molecular weight and 15.25 for the wt. % chlorine. The measured ratio of P:B in the trimer was 0.994 based on phosphorus and boron analysis of an air-hydrolyzed sample. The infrared spectrum of the trimer (in benzene) showed a sharp, moderately strong absorption band (probably P:H stretching) at 4.37 μ; relatively strong absorption bands also appeared at 6.21, 6.93, 7.25–7.50, 8.30, 8.78, 9.20, 10.35, 10.91, 11.15, 11.45, and 13.50 μ.

The trimer hydrolyzed rapidly in air. An air-hydrolyzed sample upon thermal decomposition under vacuum yielded a distillate which was approximately

20% $C_6H_5PH_2$, 60% benzene, and 20% of an unidentified product. The air-hydrolyzed (26 days) trimer (12.8 wt. % P, 4.50 wt. % B, cryoscopic molecular weight in benzene 550) gave a negative test for chlorine and a moderately strong absorption band at 4.32 μ, which is in the region for the P–H stretching vibration.

In addition to the trimer (I), a low molecular weight polymer



$$\mathrm{Cl{-}\overset{C_6H_5}{\overset{|}{B}}{-}\overset{C_6H_5}{\overset{|}{P}}{-}\overset{C_6H_5}{\overset{|}{B}}{-}\overset{C_6H_5}{\overset{|}{P}}{-}\overset{C_6H_5}{\overset{|}{B}}{-}Cl}$$

II

may also have been produced, but the data (cryoscopic molecular weight in benzene 549, 12.3 wt. % Cl; theory for compound II: mol. wt. 551, 12.9 wt. % Cl) are not adequate to prove its existence.

The products from the reaction of $C_6H_5PH_2$ and $C_6H_5BCl_2$ were dependent upon the ratio of the reactants ($C_6H_5PH_2 : C_6H_5BCl_2$). The trimer (I) was not found in measurable quantities when $C_6H_5BCl_2$ was added to a benzene solution containing excess $C_6H_5PH_2$ and the mixture refluxed. The products from the latter reaction were not identified; the infrared spectra indicated the absence of P–H bonds.

Instead of the trimer (I), Coates and Livingstone[1] identified the monomer of (I) (colorless liquid, b.p. 98–100° (*ca.* 10^{-3} mm.)) as one of the products when the xylene solution of a 1:1 complex of $C_6H_5PH_2$ and $C_6H_5BCl_2$ was boiled until evolution of HCl ceased. The explanation of why Coates and Livingstone did not obtain the trimer is not known.

Acknowledgment.—The author gratefully acknowledges analytical measurements by the Analytical staff of the G. E. Research Laboratory and the assistance of Dr. R. S. McDonald and Mr. C. Hirt in the interpretation of the infrared spectra.

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RECEIVED AUGUST 12, 1963

Carbonyl Stretching Bands of Tetracarbonyl Halide Dimers of Manganese, Technetium, and Rhenium

Sir:

The infrared spectra in the carbonyl stretching region of the molecules $[M(CO)_4X]_2$ where M = Mn, Tc, Re and X = Cl, Br, I have been reported by El Sayed and Kaesz.[1] Very recently the X-ray analysis of the structure of $[Mn(CO)_4Br]_2$ has confirmed the halogen-bridged D_{2h} structure[2] previously favored on the basis of infrared evidence.[1] The purpose of the present note is to point out that although the general conclusions of the infrared analysis are undoubtedly correct, in the author's opinion the detailed assignments are probably in error.

In the $[M(CO)_4X]_2$ structure (Fig. 1) we may distinguish two types of carbonyl, one *trans* to a halogen and the other *trans* to a second carbonyl group. General experience and in particular comparison with the manganese carbonyl monohalides[3] shows that the CO force constant must be a great deal smaller for the former type than for the latter. It is natural therefore to assign the two high frequency bands to the out-of-plane carbonyl groups and the others to the in-plane groups. If we assume only weak coupling between metal atoms we arrive, by methods outlined elsewhere,[3,4] at the assignment

A	B	C	D
$b_{3u}(a)$	b_{1u}	$b_{3u}(b)$	b_{2u}

using the notation of El-Sayed and Kaesz. It is just possible that the assignment of C and D should be reversed, but only if bond-stretching interaction constants in these compounds are very different from those usually encountered.[4]

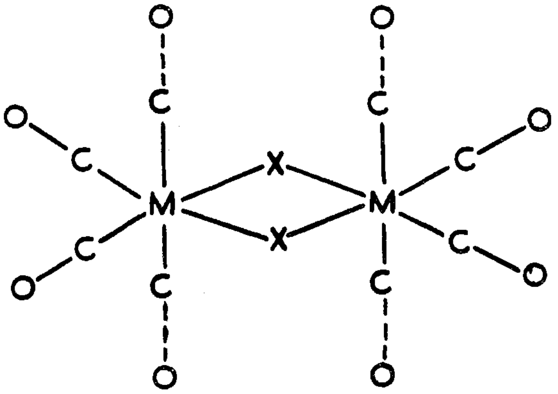

Fig. 1.—The $[M(CO)_4X]_2$ structure showing inequivalent in-plane C—O and out-of-plane C---O groups.

The assignment is preferable on the following additional grounds: (a) The behavior of the different bands on changing the halogen parallels closely that already recorded for the monohalides. (b) The almost constant frequency difference between A and B modes as the halogen is changed is explained naturally since it is predicted to depend only on the CO–CO bond-stretching interaction constants. (c) The magnitudes of the CO–CO bond-stretching interaction constants required to account for the spectrum are more in line with those for related compounds.

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(1) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

(2) L. F. Dahl and C. Weir, *Acta Cryst.*, **16**, 611 (1963).

(3) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1963).

(4) L. E. Orgel, Proceedings, International Symposium on Molecular Structure and Spectra, Tokyo, 1962, Paper A 315.

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RECEIVED AUGUST 3, 1963